



Project Summary

Sampling Carbonaceous Aerosols: A Review of Methods and Previous Measurements

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Carbonaceous aerosols, a complex mixture of carbonate carbon, elemental carbon, and organic carbon (organic compounds), are of environmental importance due to their impact on visibility and the toxicity of some of the organic compounds. A knowledge of the relative vapor and particle concentration of semivolatile organic compounds is required to understand how the compounds are transported in the atmosphere and removed by deposition. Also, the deposition in the lungs is dependent on the vapor/particle distribution. Because of the multiplicity of compounds of varying volatility in the organic aerosols, the sampling of these particles presents an extremely difficult challenge. This report, based on a literature search of measurement studies for the past 20 years, reviews the possible artifacts that can occur that result in positive and negative errors owing to volatilization, sorption, or reaction during the sampling processes.

The sampling approaches that have been used range from single filters up to complex parallel multiple component systems that employ diffusion devices to separate particle and vapors. The artifacts that were addressed by each approach are included. Representative, but not exhaustive, lists of previous carbonaceous aerosol measurements are presented based on the literature review. The first list includes measurements of elemental carbon and organic carbon without resolution of individual organic compounds. The location, measured concentrations, and comments on the artifacts addressed are presented for each study. The second list is a representative group of measurements of specific organic compounds or classes of organic compounds. Here, because of the large number of indi-

vidual compounds present, concentrations of each compound are not listed, but the artifacts that the employed sampling method addresses are noted.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Carbonaceous materials are usually a major component of ambient fine particle mass concentration. For example, carbonaceous aerosols have been found to account for typically 40% of the total fine particle mass loadings in the Los Angeles area. These particles consist of a multitude of organic compounds, both molecular and macromolecular, as well as elemental carbon. Over 2800 compounds have been identified in the ambient atmosphere, but in those studies that have quantified the individual organic compound concentrations, usually the sum of the measured compounds account for only a few percent of the total organic mass concentration.

The potential toxicity of some of the organic aerosols has made them the subject of environmental concern and extensive investigation. Special attention has been devoted to the hydrocarbon fraction owing to the mutagenic activity exhibited by compounds such as polynuclear aromatic hydrocarbons (PAHs) and their potential carcinogenic effects. The predominance of organic aerosols in the fine particle size range makes them efficient transporters of any toxic compounds into the respiratory system.

The carbonaceous aerosols, especially elemental carbon, are also of environmental concern because they occur in the visibility-reducing size range (0.1 μm –1.0 μm) and may therefore have an important impact on visibility conditions and possibly climate. Elemental (or black) carbon is the most important absorbing species for sunlight in the atmosphere, and its catalytic properties may result in its contribution to important atmospheric chemical reactions.

Elemental Carbon and Organic Carbon Aerosols

The complex mixtures of carbonaceous aerosols are often classified as carbonate, elemental carbon (EC), and organic carbon (OC) that consists of organic compounds. Ambient studies have shown that carbonates account for only a negligible fraction of the total carbon in urban aerosol. Elemental carbon has a chemical structure similar to impure graphite and is emitted directly from fossil fuel combustion sources. Optical methods have been used to measure EC, as it is considered the primary component of atmospheric aerosol that strongly absorbs light.

Organic aerosol compounds in the atmosphere may result from direct emissions from a source (primary OC) or may result from condensation of low vapor pressure products of gas phase reactions of hydrocarbons onto existing atmospheric particles (secondary OC) or the reaction product of primarily emitted organic compounds with atmospheric oxidants.

A method based on thermal/optical reflectance procedures has been used to measure the EC and OC components of ambient aerosols. Several variations of the procedure have been used that differ in respect to the analysis time, temperature ramping rates, volatilization and combustion, and calibration procedures. Variations in the measured EC and OC results of a variety of samples in an interlaboratory comparison study have been reported. In general, the agreement between laboratories for total carbon was within 20% for all samples, but there were large interlaboratory differences in the OC/EC ratio for all samples. Differences among sampling methods were compared with differences in analytical methods. For EC, the observed differences in side-by-side sampling were accounted for by differences in the analytical methods. For OC, most methods showed greater variability in results than could be accounted for by the differences in analytical methods.

Carbonaceous Aerosols Sampling Artifacts

As with most ambient aerosol measurements, the most frequently employed sampling technique for organic aerosols is collection on filters, usually quartz fiber filters. Because the organic aerosols are a complex mixture of many compounds with a wide range of vapor pressure, sorption properties, and chemical stabilities, the sampling process has the potential for several sampling artifacts. These may include the following:

- (1) A portion of the organic vapor phase may sorb onto the filter surface or on the deposited particulate matter. This is often called the "positive" artifact because the apparent mass that would be collected and measured is greater than the aerosol mass that existed in the volume of the atmosphere sampled.
- (2) The sampling process may change the gas-solid distribution of the sample being collected, which results in volatilization of some of the particulate organic compounds. This produces a negative artifact.
- (3) The collected particulate matter may chemically react with vapor components that pass through the filter during sampling to change the chemical composition of the deposit. This can result in positive or negative artifacts, especially if individual chemical compounds or chemical functionalities are being measured.

These sampling artifacts complicate the organic aerosol measurements, and it is difficult to separate the different competing artifact processes although this has been the object of many studies.

The positive artifact has been investigated extensively. For example, samples collected on a high-volume sampler quartz filter indicated a positive bias of about 15%. With 24-h samples, positive errors in organic carbon of 15–20% were found, but the degree to which this was offset by loss of volatile OC is not known. A typical glass fiber filter has a surface area that is much smaller than that of collected atmospheric particulate matter, so that sorption of vapor on the particles is believed to outweigh sorption on filters. Diminished levels of OC recovered from filters at higher sampling velocities were attributed to decreased sorption rather than increased volatilization. The negative artifact has also been investigated. Theoretical calculations have indicated that the evaporation losses are probably most important when filters with high pressure drops are encountered. Investigators who used a multiple parallel

collector with a diffusion denuder system concluded that samples from a remote location exhibited negative artifacts as large as 40 to 80%.

Changes in sample integrity have been indicated by studies on the degradation or reaction of PAH. A portion of particulate phase aldehyde has been shown to be oxidized during sampling to the corresponding aliphatic acid. Reaction of organic acids in atmospheric samples with basic components of glass fiber filter may occur.

Gas/Particle Distributions of Semivolatile Organic Compounds

A comprehensive understanding of the environmental impact of pesticides, PAH, PCB, and other semivolatile organic compounds in the atmosphere requires a knowledge of both their gas and particle concentrations. The gas/particle ratios are important in how the compounds are transported in the atmosphere and removed by deposition. Particles are quite effectively removed by rain events. Health effects also depend on the gas/particle ratios as they are related to how the compounds deposit in the lungs and exert potential toxic effects.

The earliest systems for measuring the gas/particle distributions were a particle filter (glass fiber, quartz fiber, or Teflon) followed by a solid sorbent trap such as polyurethane foam (PUF), Tenax, or XAD-2. The measurement is a severe challenge since the compounds are usually present in low levels (nanograms per cubic meter or less), and the procedure is subject to positive artifacts from vapor sorption, negative artifacts from volatilization from the filter, and degradation of compounds owing to reactions during sampling.

The potential for volatilization and sorption artifacts is related in part to the kinetics of the sorption process. The magnitude of the artifacts is dependent on the variability of the total particle concentration, the gas phase concentration, the temperature during the sampling, and the mass-transfer reaction time scales. The equilibrium vapor pressure concentration (EVC) of atmospheric compounds and the significance of the efficiency of collection of the compounds on filters have been considered. Absolute values of the absorbed state EVCs or the factor by which the pure state EVCs are commonly reduced by sorption have been deduced from measurements of losses from actual air samples. A critical evaluation of the literature gave a wide range of factors (2–500) by which the pure state was re-

duced by adsorption. This was attributed to uncertainty in the literature data rather than the difference in actual reduction factors. Comprehensive analyses have been presented of the partitioning of organic compounds between vapor and solid aerosol phases. Estimates of the slope and intercept from plots obtained from a database of gas particle distribution data vs $1/T$ were found to be useful for predicting the distribution in other urban environments. The effects of relative humidity on gas/particle partitioning have been investigated and compared to field studies. The log of the gas/particle partition constant was found to have linearly decreasing dependence on the relative humidity over the range from 40 to 85% relative humidity, based on semivolatile PAH compounds measurements at Osaka, Japan. A thermodynamic model has been developed to predict the partition between vapor and liquid phases based on two parameters: initial vapor mole concentration ratio and the ratio of Henry's Law constant to initial vapor partial pressure. As opposed to soluble organic compounds, the partially soluble organics tend to partition toward the vapor phase owing to the large Henry's Law constants.

Measurement Approaches for Sampling Carbonaceous Aerosols

Sampling methods for determining organic aerosol concentration and, if desired, the corresponding vapor phase concentration of semivolatile compounds have evolved from the simple arrangement of a single filter followed by a sorbent trap. As investigators have attempted to eliminate or quantify the various artifacts that were encountered, their sampling approaches have become more complex with various denuder arrangements, multiple combinations of filters of different sorbency (quartz, carbon impregnated, Teflon) and various sorbent traps. Sample arrangements that have been used included the following:

- (1) Filter only
This approach assumed there were neither sorption nor desorption artifacts.
- (2) Filter/sorbent
This approach was used for total (vapor plus particle) concentration but does not give correct gas/particle distributions except for non-volatile organics that are due to artifacts.
- (3) Multiple filters in series
Two quartz filters were employed back to back with the amount on the second filter used to correct the

positive artifact (vapor adsorption) on the first. The vapor concentration passing through the second filter is assumed to be essentially the same as the first, which may not be true if the vapor is strongly sorbed by the filter. Also, it does not account for the negative artifact or the amount adsorbed on the collected particles.

- (4) Dual quartz tandem filters with a parallel Teflon/quartz tandem.
This is similar to the dual filter approach above but had two parallel sets of tandem filters: the first is a quartz filter with a quartz after-filter and the second is a Teflon filter with a quartz after-filter. The positive artifact is corrected by subtracting from the quartz of the first set the amount on quartz after-filter of the second set. The rationale is that the Teflon would absorb much less of the vapor than quartz so the exposure of the quartz filter after the Teflon would be closer to the atmospheric vapor concentration.
- (5) Denuders
Diffusion denuders are devices with channels operated at laminar flow conditions in which vapors of the atmospheric sample are separated from the particles owing to the much greater diffusion coefficients of the vapors. High performance denuders, compound annular denuders that consist of coaxial cylinders so that the air samples pass through the annular space, have been designed that allow the use of higher sampling rates.

Various combinations of denuder arrangements have been employed in organic aerosol sampling. A denuder difference procedure for specific PAH compounds has been developed in which two parallel sampling arrangements are used. On one side was the sequence: denuder, quartz fiber filter, sorbent trap. On the other was quartz fiber filter, sorbent trap (without the denuder). For specific PAH compounds the method measures true particle phase, while the vapor concentration and the degree of negative artifact are determined by denuder difference calculation, not direct analysis of the denuder.

A compound annular denuder system has been employed to trap vapor constituents by the denuder difference approach. Two filter/absorbent packs were operated in parallel: one was preceded by the denuder; the other was not. The fraction of analyte that occurred in the vapor phase was determined by subtraction of

the denuder sampler results from the conventional sampler results.

Diffusion denuders consisting of separated layers of quartz filters have been used under the assumption that they remove only the gaseous organics that are normally retained on the quartz filter. This denuder was followed by a dual quartz filter pack. Comparison of the results with a parallel dual quartz pack led to the conclusion that the OC on the back filter of an undenuded filter pack is primarily a positive enhancement artifact. The approach does not address the negative artifact.

An annular denuder-based sampler, called the integrated organic vapor/particle sampler (IOVPS), has been used for the direct determination of gas and vapor semivolatile PAH compounds in tobacco smoke. Finely ground XAD-4 was used for the denuder wall coating since it has been shown to be an efficient sorbent for PAH and nicotine. The technique provides a means for determining phase concentrations for specific compounds where their collection, recovery, and analysis have been adequately demonstrated, but it is not yet applicable to total organic vapor/aerosol phase distribution and concentration measurement. Similarly, a diffusion denuder sampler made from 120 short parallel gas chromatographic (GC) tubes coated with stationary phase has been employed to measure PAH. The collected gas on the denuder was analyzed directly by desorption onto a GC column without solvent dilution. The denuder was followed by a quartz fiber filter and a PUF plug. Particles are collected on the filter. Vapor-phase molecules that break through the denuder as well as molecules that volatilize off the particles are collected on the PUF.

One of the most elaborate of the semivolatile organic sampling systems consists of three parallel samplers, two of which contain multichannel parallel plate diffusion denuders that were carbon-impregnated filter paper to collect the gas phase. Sampler 1 has the following sequences: cyclone, denuder, two quartz filters, sorbent filter (the same carbon-impregnated material used in the denuder plates) and, finally, a quartz filter. Sampler 2 is the same as Sampler 1 except the denuder is placed after the two quartz filters instead of before. Sampler 3 is only a filter pack; that is, the same as Samplers 1 and 2 but without the denuder. Conclusions drawn by the investigators from sampling with the system at Canyonland National Park are that the conventional quartz filter artifact is a negative rather than positive artifact and previous data measurements with filters may have underestimated the par-

ticulate organic carbon by more than 100%.

Survey of Carbonaceous Aerosol Measurements

Measurement of Total Organic Aerosol Concentration

A representative listing of field studies, where only the elemental carbon and total organic aerosol concentrations were determined without organic compound resolution, is presented in the report with references. Sampling techniques have ranged from single filters to complex, parallel multicomponent sampling systems.

Measurement of Specific Organic Compounds

A list of studies in which individual compounds or classes of compounds have been specifically identified and measured is also presented in the report with references. Owing to the large number of studies on pesticides, PCB, and PAH compounds, the full report does not present a comprehensive listing of all measurements that have been made. Also,

the sum of the concentrations of the resolved compounds in most of the studies does not account for more than a few percent of the total organic mass. Because many compounds in these specific organic classes exist as both vapor and particles their measurement involves the same sampling and artifact problems encountered with total organic aerosol measurements.

Conclusions

The sampling of organic aerosols in the atmosphere is an extremely difficult task owing to the very complex composition of its organic molecular constituents. Examination of the peer-reviewed literature for organic aerosol sampling studies during the last 20 years yields the following observations:

- (1) A large percentage of the reported measurements are subject to artifact errors. In a few cases the investigations ignore the artifacts, in some they are acknowledged but unaddressed, and in other studies attempts are made to estimate the magnitude of the artifacts by vari-

ous sampling designs, many of which yielded results that were later challenged.

- (2) In studies where the investigators attempted to measure the sampling error, the magnitudes of the determined positive or negative artifacts have varied considerably. This is probably due, in part, to differences in the organic molecular composition (hence in the relative volatilities and sorptivities) and in the concentrations that occurred at the different sampling locations.
- (3) Multiple component sampling systems employing vapor phase separation devices such as denuders require a thorough evaluation to demonstrate efficient removal of the vapor at the operating conditions. This has been done for specific PAH compounds. However, the application of their multiple component system to the determination of total OC aerosol for mixtures of atmospheric organic compounds presents a formidable challenge.
- (4) The use of paired, parallel samplers (denuder difference method) is subject to the propagation of errors through subtraction, which degrades the precision. More development work with control experiments needs to be done on a wide range of organic compounds and concentrations before the sampling approach becomes credible for extended field studies.

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The complete report, entitled "Sampling Carbonaceous Aerosols: A Review of Methods and Previous Measurements," (Order No. PB95-129060; Cost: \$17.50, subject to change) will be available only from
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